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A study of toluyl imino malonate

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A STUDY OF TOLUYL IMINO MALONATE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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A STUDY OF TOLUYL IMINO MALONATE.

Introduction.

A number of papers have appeared in the journals on the reaction products of malonic ester as worked out in this laboratory[1].

The starting point for this research has been ethyl dihydroxymalonate, $HO \diagdown C \diagup CO_2C_2H_5$ $HO \diagup \quad \diagdown CO_2C_2H_5$. This compound is best prepared by method of Curtiss[2].

Curtiss and Spencer[3] treated methyl dihydroxymalonate with P_2O_5, and obtained pure anhydrous methyl oxomalonate, $O = C \diagup CO_2C_2H_5$ $\diagdown CO_2C_2H_5$, by fractional distillation under reduced pressure[3]. This method was used in this work.

Spencer[4] working with methyl oxomalonate, and Hill[5] with ethyl oxomalonate, formed a number of addition products by action of alcohols and amines on ketone esters:-

$$C_2H_5OH + O = C \diagup COOCH_3 \quad \diagdown COOCH_3 = C_2H_5O \diagdown C \diagup COOCH_3 \quad HO \diagup \quad \diagdown COOCH_3 \qquad (3)$$

$$CH_3C_6H_4NH_2 + O = C \diagup COOC_2H_5 \quad \diagdown COOC_2H_5 = CH_3C_6H_4OH \diagdown C \diagup COOC_2H_5 \quad HO \diagup \quad \diagdown COOC_2H_5 \qquad (5)$$

(1) Curtiss. J. Am. Chem. Soc., 19, 691; 18, 435; 22, 509; 28, 315; 30, 133; 33, 603; 35, 354; 35, 477; 30, 1264; 31, 1053.
(2) Ibid., 33,603.
(3) Ibid., 31, 1053.
(4) U. of I. Thesis, M. S., 1909.
(5) U. of I. Thesis, B. S., 1909.

When these addition products are formed with oxomalonates, the green color of the ketone esters disappears, resulting in the formation of colorless bodies. This color change has been explained by the theory of Baly, Stewart, and Deseh[1] which aims to account for the cause of color in organic bodies. The change of color, they say, depends upon the rapidly oscillatory vibrations of supplementary valencies that are adjacent. These vibrations are of such a character as to produce vibrations in the ether of the same characters as those which produce spectrum color.

Ethyl paratotuidinotartronate loses water by action of P_2O_5 to form Ethyl Toluyl Imino Malonate which is a greenish yellow oil. In this dehydration product the color phenomenon is dependent upon the three adjacent unsaturated carbon atoms which act as a chromophore:-

$$O = C - (OC_2H_5)$$

$$CH_3C_6H_4N = C$$

$$O = C - (OC_2H_5)$$

This is proven by the fact that whenever the central carbon atom has its valencies satisfied, as it does in the hydrated addition product, the compound is colorless. It is only when the doubel bond N = C is formed by dehydration that the greenish yellow color appears.

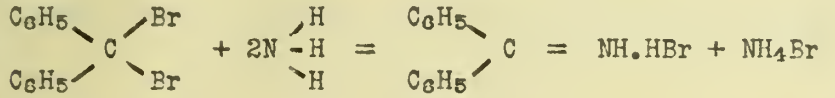
Spencer[2] succeeded in obtaining methyl phenyliminomalonate by action of P_2O_5 on methyl anilinomalonate:-

This substance is very reactive at point of double union of nitrogen and carbon, and appears to be an analogue of phenyl isocyanate.

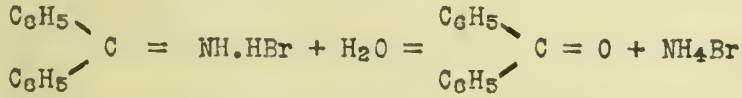
(1) J. Chem. Soc. 85, 1029; 87, 766.
Proc. Chem. 22, 33.
(2) J. Am. Ch. Soc., 31, 1053.

All efforts to dehydrate the pure ethyl para and ortho toluidinotartronate proved unsuccessful until the action of phosphorus pentoxide, P_2O_5, was tried in a sodium dry ethereal solution of the para compound. A bright greenish yellow oil was obtained which turned white on standing in air. Aniline, acting on the dehydrated product produced a vigorous heat reaction giving a baautiful crystalline body.

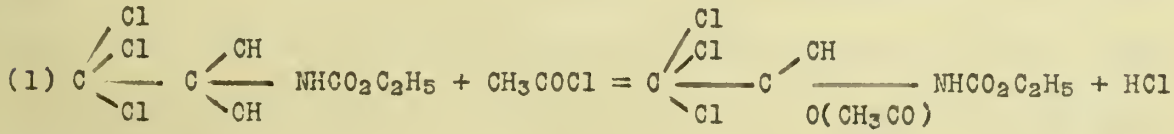
J. Moore[1] obtained a compound containing the double bond N = C by action of dried ammonia gas on diphenyl dibrommethane.

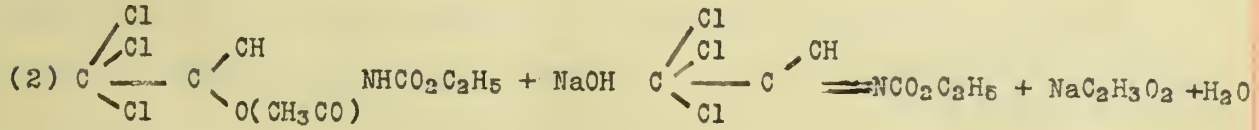


This salt, in the presence of a mere trace of water, decomposes at point of double union with the formation of the ketone

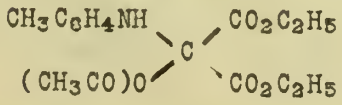


O. Diels and Carl Seib[2] obtained the Anhydro Chloral Urethane by first forming the Acetyl Chloral Urethane by action of acetyl chloride, and then treating the latter with NaOH:-





In like manner I succeeded in obtaining a compound of structure:-



but was not successful in dehydrating it.

(1) Ber. 43, 563.
(2) Ibid., 42, 4062.

The reactions with phosphorus trichloride on ethyl para and ortho toluidinotartronate were tried. In both cases, there was heat generated and a yellow chromophore obtained; but the products were too unstable to analyze. Since the crystalline body obtained was soluble in water, liberating free para toluidin on addition of potassium carbonate it is possible that the hydrochloride salt of toluyl imino malonate

$$CH_3C_6H_4NHCl = C\begin{matrix}\diagup CO_2C_2H_5 \\ \diagdown CO_2C_2H_5\end{matrix}$$

was formed which decomposed in the presence of H_2O at point of doubel union. This reaction is being further studied.

Experimental.

Preparation of Pure Anhydrous Ethyl Oxomalonate.-Twenty-five grams (one mol.) of pure ethyl dihydroxymalonate, prepared by method of Curtiss[1] were thoroughly mixed with 19 grams (3 mol.) of phosphorus pentoxide in a distilling bulb and allowed to stand airtight for an hour. At the end of this time, the mixture had taken on a yellow color and a small amount of yellow oil had separated out. At the end of twenty-four hours, the yellow oil which had separated out of the thick gummy mass was extracted with dry ether. After evaporating off the ether the yellow oil was further purified by fractional distillation under reduced pressure. Pure ethyl oxomalonate distils at a constant temperature and pressure of

Ethyl oxomalonate, $O = C\begin{matrix}\diagup CO_2C_2H_5 \\ \diagdown CO_2C_2H_5\end{matrix}$, is a greenish yellow oil having a specific gravity of 1.1192. On account of the exceedingly reactive carbonyl

(1) J. Am. Ch. Soc., 33, 603.
(2) Strachan, U. of I., M. S. Thesis, 1910.

group it rapidly changes into dehydroxymalonate on exposure to the air. It has been found to react vigorously with ammonia, hydrochloric acid, amines and other compounds containing a hydrogen atom which is easily dissociated.[1]

Action of Amines on Ethyl Oxomalonate.

Ortho Toluidin[2] on Ethyl Oxomalonate.-3.22 grams of ortho toluidin were added from a pipette to 5.90 grams of ketone ester (mol. quantities). The temperature rose to 81° C and the reaction was vigorous. The mixture was gradually cooled, and it thickened to a honey like consistency as the greenish yellow color disappeared. The mass suddenly crystallized in balls of radiating needles which were colorless. The substance was dissolved in hot ethyl alcohol, chilled to -18° C and the crystals which formed were filtered, washed with cold absolute alcohol and dried in the air.

Ethyl ortho toluidinotartronate, $CH_3C_6H_4NH \diagdown C \diagup CO_2C_2H_5$ (HO on C, $CO_2C_2H_5$ on C), melts at 92° C without decomposition. It crystallizes in bunches of radiating needles. It is easily soluble in ether, hot ethyl alcohol, chloroform, carbon tetrachloride, benzene and carbon bisulphide. In ligroin and cold ethyl alcohol it is slightly soluble.

Para Toluidin on Ethyl Oxomalonate.-3.91 grams of para toluidin, dissolved in 8 cc. of dry ether was added to 6.34 grams of ketone ester (mol. quantities) A vigorous reaction took place and the color rapidly faded out. The mixture had completely solidified in five minutes. The product was recrystallized from absolute alcohol, filtered at the pump and dried in the air.

Ethyl para toluidinotartronate, which is colorless melts at 95° C., giving a yellowish white body when solidified. It crystallizes in bunches of radiating needles. It is easily soluble in ether, hot ethyl alcohol, benzene, chloroform, carbon tetrachloride, and carbon bisulphide. It is slightly soluble in cold ethyl alcohol and ligroin. All solutions of this compound have a

(1) Strackan, U. of I., M. S. Thesis, 1910.(2)Hill, U. of I., B. S. Thesis, 1909

very faint yellow tinge which solutions of the ortho toluidinotartronate do not possess.

Small portions of the two tartronates, spread on watch crystals in a vacuum dessicator over sulphuric acid, showed only a few yellow patches after two months.

Action of Phosphorus Pentoxide on Ethyl Para and Ortho Toluidinotartronate.

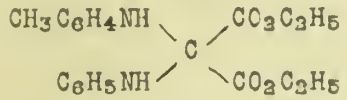
Action of Phosphorus Pentoxide in Dry Ether.-0.4 grams of phosphorus pentoxide (about 3 mols.) were added to 1 gram of ethyl para toluidino tartronate which was dissolved in 10 cc. of dry ether. At the end of three days the mixture had taken on a deep yellow color. The ethereal solution above the gummy phosphoric acid residue, which had an appearance similar to the residue left by dehydration of methyl anilino malonate[1], had a greenish yellow tinge. The ether was evaporated off in a vacuum dessicator, leaving a thick greenish oil.

This greenish yellow oil when rubbed with glass rod in closed test tube does not crystallize; but when exposed to the air it slowly whitens, as in the case of methyl phenyliminomalonate[2], and on rubbing with a platinum spatula in 15 minutes the glycerine like liquid suddenly crystallized as in the form of radiating needles. The solubility tests, the crystalline forms, and the melting point determination showed this body to be ethyl para toluidinotartronate. This suggests that the greenish yellow oil has hydrated at the point of double union of carbon and nitrogen by the action of the moisture of the air and produced ethyl para toluidinotartronate:-

$$CH_3C_6H_4N = C(CO_2C_2H_5)(CO_2C_2H_5) + H_2O \qquad CH_3C_6H_4NH\,C(HO)(CO_2C_2H_5)(CO_2C_2H_5)$$

(1) and (2) J. Am. Ch. Soc., 32, (1910).

0.2 cc. of the greenish yellow body was pipetted into a small test tube and 0.2 cc. of dry aniline was added. The greenish yellow color immediately disappeared with great evolution of heat. At the end of two hours the mass had solidified. It was recrystallized twice from carbon bisulphide, and melted at

Calculated for 

C H N

Found C H N

Action of Phosphorus Pentoxide.-Para and ortho toluidinotartronate were mixed with phosphorus pentoxide in proportion from 1 to 4 mols, and the mixtures were subjected to various degrees of heat from 20° C to 150° C for from 5 minutes to an hour in order to influence dehydration. In every case there was a yellow color formed; but on extraction with dry ether, the dissolved substance on crystallizing out proved to be the crude hydrated addition products.

Distillation of Ethyl Para Toluidinotartronate with Phosphorus Pentoxide.-3 grams (1 mols.) of ethyl para toluidinotartronate were thoroughly mixed with 2 grams of phosphorus pentoxide (about 2 mols.) in a distilling bulb. After standing three weeks, the mixture had become dark yellow in color and very sticky. When distilled under reduced pressure, the mass gradually darkened as the temperature rose. Fumes were evolved and a redish brown oil passed over. This product on standing two weeks in a dessicator went solid but would not be purified.

Action of Acetic Anhydride on Ethyl Para Toluidinotartronate.

One and five tenths grams of acetic anhydride (slight excess)was added, drop by drop, by means of a pipette to 3 grams of the para compound. As the two substances met, the mixture became deep yellow with a rise in temperature from 18° C to 35° C. The mass became semisolid, and on standing for a few hours it completely solidified. It was dissolved in 20 cc. of ether and shaken in a separatory funnel with 1 o/o sodium hydroxide solution to remove excess of the anhydride. The ethereal solution was drawn off, dried over calcium chloride and the ether evaporated. The crude produce obtained was recrystallized from hot benzene. It melted at 150° C.

Calculated for $CH_3C_6H_4NH\diagdown C\diagup CH_3COO$ $\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$ or $CH_3C_6H_4N(OC_2H_3)\diagdown C\diagup HO$ $\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$

	C	H	N
	59.45	6.50	4.34
Found	59.66	6.71	4.37
	59.42	6.82	4.42

Acetyl ethyl para toluidinotartronate crystallizes in beautiful needles of satin lustre. It is easily soluble in ether, hot benzene, hot ethyl alcohol, chloroform, and carbon bisulphide, and slightly soluble in cold benzene, ligroin and ethyl alcohol.

Action of Phosphorus Trichloride on Ethyl Para Toluidinotartronate.

0.16 grams of phosphorus trichloride was added to 1 gram of the para compound. A slight heat reaction took place, and the mixture immediately turned yellow. The mass was heated to complete the reaction. After extracting with

ether, the insoluble residue was filtered off. In a few moments there was a precipitation in the filtrate. By adding an excess of ether, this separation was avoided. When ether extract was evaporated, yellow precipitation occurred. This yellow body when washed with ether on porous plate turned white with liberation of a gas. The residue on the filter, and the crystalline body from ether extract were both soluble in water, free toluidin was liberated in the form of an emulsion when potassium carbonate was added. It is possible that the hydrochloride salt of Toluyl Imino Malonate, $CH_3C_6H_4NHCl = C\begin{matrix}\nearrow CO_2C_2H_5 \\ \searrow CO_2C_2H_5\end{matrix}$, is formed which in the presence of H_2O breaks up at the point of double union giving toluidin hydrochloride and the ketone ester which with the excess of water forms ethyl dihydroxymalonate. This reaction is analogous to the reaction of methyl phenyliminomalonate with water[1].

This reaction and the composition of the aniline addition on Toluyl Imino Malonate are being studied.

(1) J. Am. Chem. Soc., 32, (1910).